Influence of a fractured medium on pyrite oxidation reaction

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Contents

1 Context

2 Reactive model

3 Reactive transport

4 Domain

5 Tests cases

1. Context
   - Underground Research Laboratory Meuse/Haute-Marnes
   - Excavation Induced Fractures
   - Objectives
2. Reactive model
   - Pyrite oxidation reaction
   - Completed reaction
   - Total concentration
   - Practical
3. Reactive transport
   - Coupling reactive transport model
   - SNIA
4. Domain
   - Physical domain
   - Domain Boundaries conditions
   - Domain initial condition and fractures
5. Tests cases
   - Transport reactive movie
   - Method

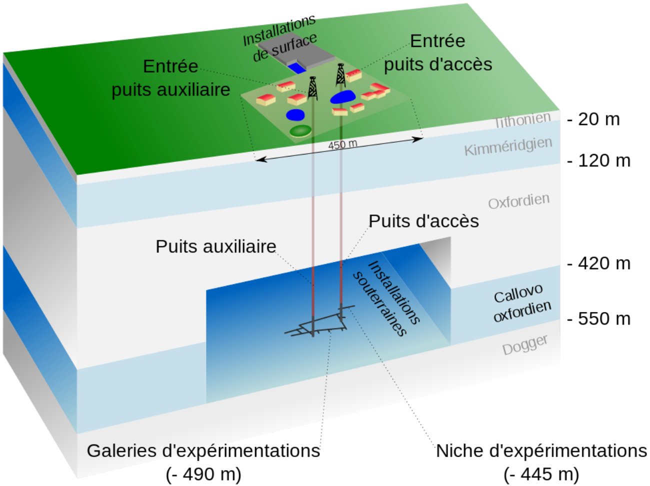

Figure: Plan of the Underground Research Laboratory (URL) at Bure, Haute Marne (from Andra)

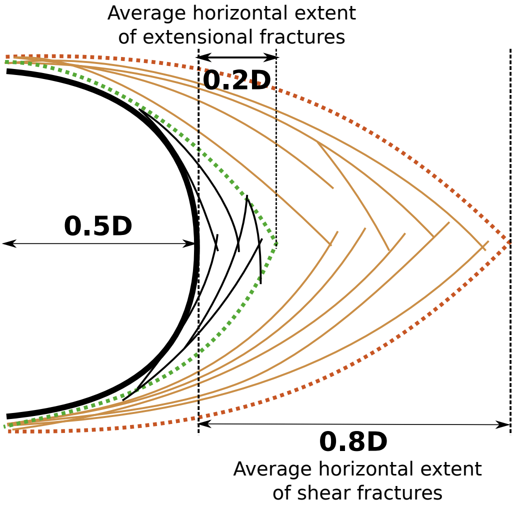

Figure: Excavation Induced Fractures at the Bure URL (adapted from)

Goals of the research project

1. A robust numerical model to represent the chemistry
2. Efficient reactive transport modeling
3. Considering fractures networks

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2 Reactive model
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3 Reactive transport
- Coupling reactive transport model
- SNIA

4 Domain
- Physical domain
- Domain Boundaries conditions
- Domain initial condition and fractures

5 Tests cases
- Transport reactive movie
- Method

Pyrite oxidation reaction

Consider the following Pyrite oxidation equation:

$$FeS_{2(p)} + H_2O_{(l)} + 3.5O_2 \rightarrow Fe^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 2H^{+}_{(aq)} \tag{1}$$

where:

- $FeS_{2(p)}$:pyrite
- $H_2O_{(l)}$: water (in excess)
- O_2: dioxygen
- $Fe^{2+}_{(aq)}$: iron ion
- $SO^{2-}_{4(aq)}$: sulfate ion
- $H^{+}_{(aq)}$: hydrogen ion

Classic approach precipitate

Appearance and disappearance of the mineral are governed by saturation threshold defined by:

$$\kappa_p - \gamma_i(c)$$

where $\gamma_i(c) = \prod_{k=1}^{N} c_k^{E_{ik}}$ is the solubility product and κ_p is the constant of solubility. So there are two possible cases, either the fluid is under-saturated and the mineral can be dissolute:

$$p_i = 0,\ \kappa_p - \gamma_i(c) > 0,\ \forall i = 1, ..., N_p$$

or the fluid is saturated and the mineral is present

$$p_i \geq 0,\ \kappa_p - \gamma_i(c) = 0,\ \forall i = 1, ..., N_p$$

Pyrite case

The solubility product to the pyrite oxidation is:

$$\gamma = \frac{[Fe^{2+}][SO_4^{2-}]^2[H^+]^2}{[O_2]^{3.5}}$$

Moreover, the constant of solubility κ_p is greater ($\geq 10^{200}$) so fluid is always under-saturated.
So to avoid these drawbacks we introduce a simpler model.

Overall reaction

Definition

A reaction is completed if one of its reagents disappears at equilibrium.

For example:

$$p_o + \alpha c_o \to \sum \alpha_i c_i$$

At equilibrium:
p_o or c_o equal to 0

Hypothesis

Only one precipitate and one aqueous substance are reagents of the completed reaction

Under this hypothesis we can rewrite on a complementarity problem

$$\left\{ \begin{array}{l} c_o . p_o = 0 \\ c_o \geq 0 \quad p_o \geq 0 \end{array} \right. \tag{2}$$

Total concentration

In addition, the model is completed by the mass balance equation.

$$t_o = c_o - \alpha p_o \tag{3}$$

Finally, combining (2 and 3) gives the geochemical model.

$$\begin{cases} t_o = c_o - \alpha p_o \\ c_o . p_o = 0 \\ c_o \geq 0 \quad p_o \geq 0 \end{cases} \tag{4}$$

The unique solution of (4) is
If $t_o > 0$:

$$c_o = t_o \quad p_o = 0$$

If $t_o < 0$:

$$c_o = 0 \quad p_o = \frac{t_o}{-\alpha}$$

where α is stoichiometric coefficient (here $\alpha = 3.5$).

Practical

	$FeS_{2(p)}$	O_2
Equilibrium State	0.43	0
Phreeqc Result	0.43	0

Table: Pyrite disappearance (T=-1.5)

	$FeS_{2(p)}$	O_2
Equilibrium State	0	1.65
Phreeqc Result	0	1.65

Table: Oxygen disappearance (T=1.65)

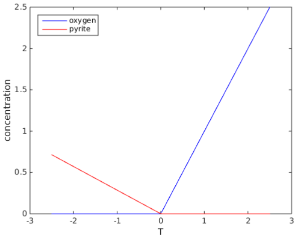

Figure: Results overall equation

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   - Underground Research Laboratory Meuse/Haute-Marnes
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   - Pyrite oxidation reaction
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   - Total concentration
   - Practical
3. Reactive transport
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   - Physical domain
   - Domain Boundaries conditions
   - Domain initial condition and fractures
5. Tests cases
   - Transport reactive movie
   - Method

Coupling reactive transport model

In geological waste disposal, the transport is driven by the diffusion. The coupling reactive transport model is:

$$\left\{ \begin{array}{l} \partial_t t_o - d\Delta c_o = 0 \\ t_o = c_o + \alpha_o p \\ c_o.p = 0 \\ c \geq 0 \quad p \geq 0 \\ +IC \quad +BC \end{array} \right. \tag{5}$$

d $\in \mathbb{R}^+$: diffusivity coefficient

Coupling reactive transport model

Considering now, the overall reaction where Nc aqueous components are present, the coupling reactive transport model becomes:

$$\begin{cases} \partial_t t_o - d\Delta c_o = 0 \\ t_o = c_o + \alpha_o p \\ c_o.p = 0 \\ c_o \geq 0 \quad p \geq 0 \end{cases} \tag{6}$$

$$\begin{cases} \partial_t T_i - d\Delta C_i = 0 \quad i = 1...Nc-1 \\ T_i = c_i + \alpha_i p \quad i = 1...Nc-1 \\ +IC \quad +BC \end{cases} \tag{7}$$

where:
$\mathrm{T} \in \mathbb{R}^{Nc-1}$
$\mathrm{C} \in \mathbb{R}^{Nc-1}$

SNIA

A sequential non-iterative approach is used to discretize the system (5).
An Euler explicit method is used in time and a difference finite in space.
Let N_m the number of nodes on the mesh.

$$
\begin{cases}
\frac{t_o^{n+1}-t_o^n}{\delta t} - d\ Lc_o^n = 0 & \\
t_o^{n+1} = c_o^{n+1} + \alpha_0 p^{n+1} & i = 1...N_m \\
c_o^{n+1}.p^{n+1} = 0 & i = 1...N_m \\
c_0^{n+1} \geq 0 \quad p^{n+1} \geq 0 & i = 1...N_m \\
+IC \quad + BC &
\end{cases}
$$

Notations:

L is the discretized space operator.

SNIA

A sequential non-iterative approach is used to discretize the system (5). An Euler explicit method is used in time and a difference finite in space. Let N_m the number of nodes on the mesh.

$$\begin{cases} \frac{t_o^{n+1}-t_o^{n}}{\delta t} - d\ Lc_o^n = 0 & \\ t_o^{n+1} = c_o^{n+1} + \alpha_0 p^{n+1} & i = 1...N_m \\ c_o^{n+1}.p^{n+1} = 0 & i = 1...N_m \\ c_0^{n+1} \geq 0 \quad p^{n+1} \geq 0 & i = 1...N_m \\ +IC \quad + BC & \end{cases}$$

Remarks:

- The chemistry system and the transport system are decoupled
- Easy parallelization in component for transport and in nodes for chemistry
- CFL condition (Euler explicit) simple geometry (difference finite)

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   - Practical
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Physical domain

Symmetries allows to model only a quarter of the gallery.
Fractures, typically, measure centimeters.

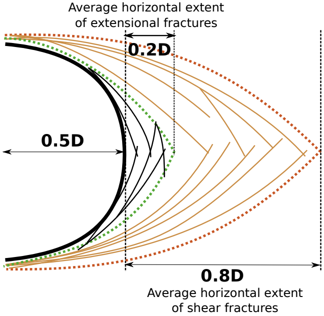

Figure: Excavation Induced Fractures at the Bure URL (adapted from)

Fractures model

Fractures are considered like fixed nodes. However fractures should be connected to the gallery.

Domain Boundaries conditions

The mesh is common for every components, only boundaries' conditions may be different.
Set the simulation time and the diffusivity's coefficient.

- Domain settings such as oxygen values are zeros on the right boundary
- Left boundary is the gallery and values of oxygen are set (Dirichlet boundary)
- Top and bottom boundaries are Neumann conditions (no flux)

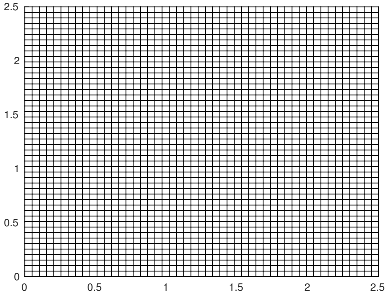

Figure: Mesh

Domain initial condition and fractures

The mesh is of the order of centimeters.

- no oxygen in the domain at the initial state
- the pyrite is present on some nodes
- some nodes are setting like fractures (fixed value)

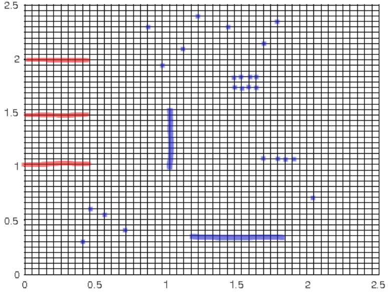

Figure: Mesh

1. Context
   - Underground Research Laboratory Meuse/Haute-Marnes
   - Excavation Induced Fractures
   - Objectives
2. Reactive model
   - Pyrite oxidation reaction
   - Completed reaction
   - Total concentration
   - Practical
3. Reactive transport
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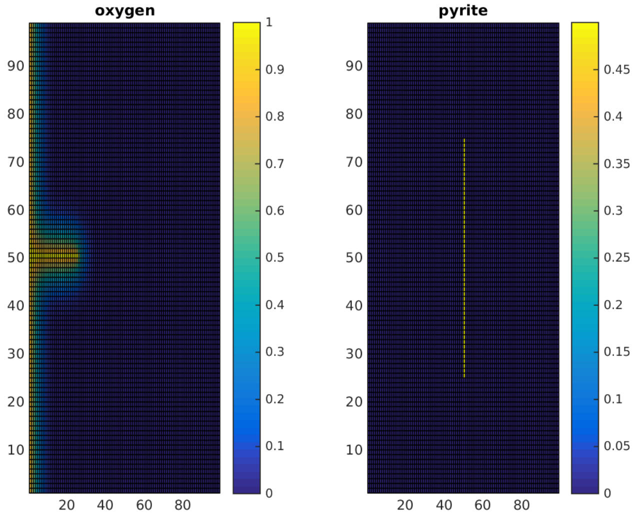
Test 1


oxygen
pyrite
90
80
70
60
50
40
30
20
10
20
40
60
80
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0

Method

We will set a quantity of pyrite and a simulation time, such as, a significant quantity of pyrite will be dissolve and we will look at these criteria:

- pyrite density
- pyrite localization
- several fractures

On the following slides:

- The simulation time is fixed
- Initial quantity of pyrite is constant
- Size of the fracture is constant

On other words, only position, density pyrite change as fractures' length and position.

Test 2

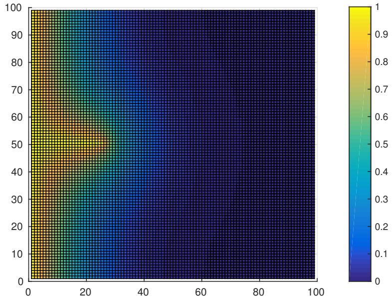


Figure: Diffusion

	oxygen quantity	pyrite quantity
Initial State	25	0
Result	$1.89 * 10^3$	0

Table: Example 2

Test 3

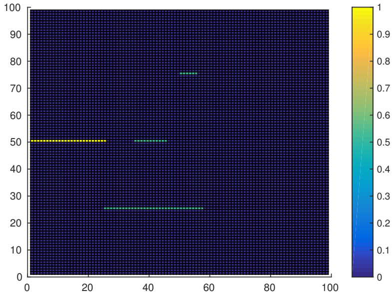


Figure: IC + BC

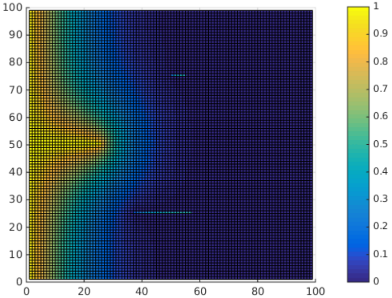


Figure: Result

	oxygen quantity	pyrite quantity
Initial State	25	25
Result	$1.84 * 10^3$	10.668

Table: Example 3

Test 4

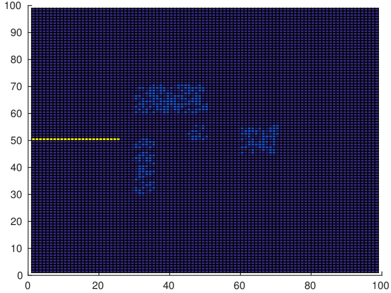


Figure: IC + BC

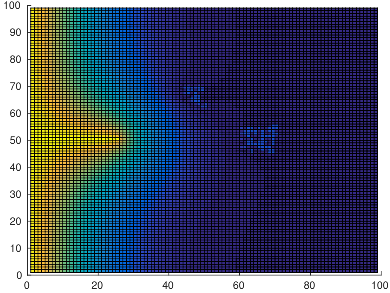


Figure: Result

	oxygen quantity	pyrite quantity
Initial State	25	25
Result	$1.84 * 10^3$	7.95

Table: Example 4

Test 5

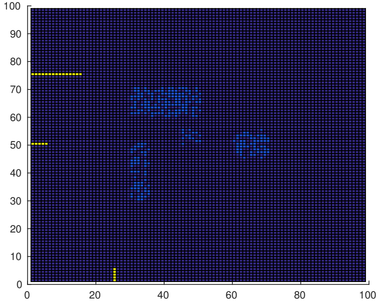


Figure: IC + BC

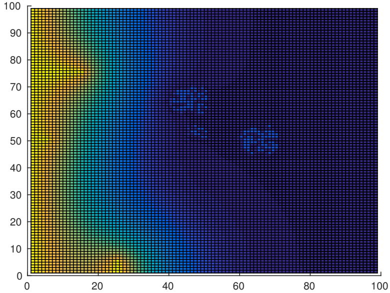


Figure: Result

	oxygen quantity	pyrite quantity
Initial State	25	25
Result	$1.87 * 10^3$	11.90

Table: Example 5

Conclusion and future work

Conclusion

Position, density and number of fracture have a great influence on the oxygen infiltration.

Future work

- consider more reaction
- more accurate fracture model
- Global DAE approach
- adaptive mesh refinement